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Inorganic Qualitative Analysis in Freshman Chemistry

Theodore S. Prokopov

Upper Iowa College

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THEODORE S. PROKOPOV[1]

Abstract. A nonsulfide scheme of inorganic qualitative analysis is presented, using solutions of hydrochloric acid, sodium acetate, sulfuric acid, and sodium hydroxide as group reagents. The identification of ions is performed by microscopic examination of crystals formed and also by employing color reactions (spot tests).

The purpose of this new approach to qualitative analysis is to eliminate the disagreeable odor and corrosive action of hydrogen sulfide and also to achieve more sharp separation of groups. The new scheme with its crystalloscopic and coloriscopic reactions lead to much more certain analytical results.

It is generally accepted that General Chemistry can be taught more effectively in qualitative analysis than in any other course and therefore efforts should be made to strengthen this subject. Accordingly, the second term of General Chemistry in most colleges and universities is accompanied by experimental qualitative analysis.

A strong opinion is also expressed that a qualitative analysis should teach analysis, e.g., should not only support the theoretical part of general chemistry but also teach analytical methods and techniques that could be applied later in the industrial and research laboratory.

The usual procedure in a systematic analysis of mixtures is the separation of cations into groups by means of group reagents prior to their identification. This method is convenient even if all the specific reagents for all ions were available, for a complicated problem is subdivided into less complicated ones, and in many cases some groups of ions may be absent from a sample and all reactions for all possible ions need not be tried.

Although Boyle drew attention to numerous qualitative tests and used hydrogen sulfide for detection of tin and lead in aqueous solutions and Bergman, Klaproth, and Pfaff used H_2S as a reagent for the separation of metals, chemists are indebted to Fresenius for a systematized hydrogen sulfied system of qualitative analysis.

His was undoubtedly one of the most successful books on analytical chemistry ever written. By his death in 1897, the book had reached 16 editions. Three years after its first appearance, English, French, Italian, Dutch, Spanish, Hungarian, even Chinese and later, Russian editions were published.[1] When we read this book, we feel it to be a modern textbook of qualitative analysis. This feeling is quite natural as qualitative analysis even today is

[1] Upper Iowa College, Fayette, Ia. 52142.

written, taught and carried out according to the system of Fresenius.

But this system is not perfect. H_2S (no matter from what source it comes) is a poisonous, highly unpleasant and corrosive gas. Its corosive action cannot be toleated in a laboratory with expensive equipment. This objection is nearly as old as the Fresenius system itself. There is another, more important drawback which cannot be tolerated: it is the uncertainty of results of the analysis.

Excess nitrate ions, or any oxidizing ions, oxidize H_2S to sulfur and sulfuric acid, which causes precipitation of Ba^{++}, Sr^{++}, and Ca^{++} along with Group II sulfides. Also adjusting pH prior to precipitation of Group II is crucial step in analysis. In a solution of low pH, lead, cadmium and tin will precipitate in Group III and interfere with analysis. At higher pH zinc will precipitate in Group II but the arsenate ion will not precipitate in this group but will bring down the insoluble arsenates of barium, strontium, and calcium in Group III when the solution is made basic to precipitate this group. Thus, lead, cadmium, arsenic, barium, strontium, calcium and zinc can be completely "lost" either by reason of high nitrate ion concentration or by improper acidity of the solution.

To eliminate troubles caused by "stinking" chemistry and to increase efficiency and certainty of analytical results, the author has employed a nonsulfide scheme, using solutions of hydrochloric acid.

TABLE 1. CLASSIFICATION OF CATIONS

Group	Ions in the group	Group reagent	Group precipitate
I	NH_4^+, Na^+, K^+	none	none
II	Ag^+, Hg_2^{++}, Pb^{++}	dilute HCl	$AgCl$, Hg_2Cl_2, $PbCl_2$
III	Bi^{3+}, Sb^{+3}, Sn^{4+} Fe^{3+}, Al^{3+}, Cr^{3+}	sodium acetate solution	$BiOCl$, $SbOCl$, H_2SnO_3, $Fe(OH)_2Ac$ $Al(OH)_2Ac$, $Cr(OH)_2Ac$*
IV	Ba^{++}, Sr^{++}, Ca^{++}, Pb^{++}	dil. H_2SO_4 + C_2H_5OH	$BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$
V	Hg^{++}, Cu^{++}, Cd^{++}, Fe^{++} Mn^{++}, Co^{++}, Ni^{++}	dilute NaOH solution	HgO, $Cu(OH)_2$, $Cd(OH)$, $Fe(OH)_2$ $Mn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$
VI	Mg^{++}, As^{3+}, Sn^{++}, Zn^{++}	none	none

*Although in pure solutions of chromium (III) salts basic acetate does not form a precipitate on boiling, by adjusting the pH with ammonia or in the presence of Fe^{3+} or Al^{3+} ions chromium (III) precipitates.

sodium acetate, sulfuric acid, and sodium hydroxide as group reagents. This new system includes also crystalloscopic and coloriscopic reactions.

Analysis of a General Unknown

Preliminary tests

Tests for Group I and for some other cations for which there are specific reactions should be made in separate portions of the original solution.

1. Tests for MnO_4^-, $CrO_4^=$ or $Cr_2O_7^=$ and their reduction (if they are present) to cations are carried out as usual.
2. The NH_4^+ is detected either by evolution of NH_3 or by crystal reaction with H_2PtCl_6 under the microscope.
3. Test for Na^+ on a slide with zinc uranyl acetate. A drop of dilute test solution is evaporated to dryness, and the residue is treated with the reagent. The crystals are examined under the microscope.
4. Test for K^+ with 70% $HClO_4$ also on a slide. Evaporate a drop of dilute test solution to dryness and treat the residue with the reagent. Observe the crystals under the microscope.
5. Test for Mn^{++} by its oxidation to MnO_4^- with KIO_4. An excess of reagent should be added.
6. Test for Cr^{+3} by its oxidation to $Cr_2O_7^=$ with $K_2S_2O_8$ (without Ag^+ as catalyst) in an acidic medium, and then convert it to CrO_5 with H_2O_2 or test the dichromate with diphenylcarbazide. The latter test is more sensitive. The addition of HCl or NaCl will eliminate the interference of Hg^{++}. The oxidation of Cr^{3+} in acidic medium is preferred in order to avoid the messy precipitate of many metal hydroxides.
7. Tests for Fe^{++} and for Fe^{3+} are carried out as usual.
8. Test for arsenic by the Bettendorf test. Mix a test drop in a micro crucible with a drop of 10% H_2O_2, and a drop of $MgCl_2$ solution. Evaporate the mixture slowly and then strongly ignite it. The arsenic is thus converted into $Mg_2AS_2O_7$. The mercury salts (if present) are volatilized. Now mix the residue with two drops of saturated solution of $SnCl_2$ in concentrated HCl and warm gently. Brown-black precipitate confirms the presence of arsenic.
9. Test for Hg^{++} with diphenylcarbazide in 0.2 N HNO_3. If $CrO_4^=$ is present, reduce it to Cr^{3+}. It could be tested also on $SnCl_2$ paper with aniline.
10. Test for Sn^{++} with $HgCl_2$ and aniline[2]. In a basic medium the reduction of Hg^{++} to Hg will occur even in the presence of traces of Sn^{++}. This reaction takes place even in such a weak basic medium as that formed by addition of aniline. A strip

TABLE 2. ANALYSIS OF GROUP III

The pH of supernate from Group II separation is adjusted with aqueous ammonia until the last drop will produce a slight turbidity. A saturated solution of sodium acetate is then added and the mixture is heated in boiling water for 10 minutes, centrifuged and checked for complete separation by repeating the procedure. Centrifuged residue is washed with 1 F NH_4NO_3.

Precipitate: $BiOCl$, $SbOCl$, H_2SnO_3 $Fe(OH)_2Ac$, $Al(OH)_2Ac$, $Cr(OH)_2Ac$ Add 6 N HNO_3, stir, warm and centrifuge. Repeat the addition of HNO_3. Combine the supernates. Wash the precipitate with 1 F NH_4NO_3.	Solution: cations of group IV, V, and VI.

Precipitate: $SbOCl$, H_2SnO_3 Dissolve in HCl	Solution: Bi^{3+}, Fe^{3+}, Cr^{3+}, Al^{3+} Make strongly alkaline with NaOH and add H_2O_2 (carbonate-free)

$SbCl_4^-$ Test with Rhodamine B; confirm with CsCl + KI under the miscroscope.	$SnCl_6^=$ Reduce to Sn^{++} and test with $HgCl_2$; confirm with CcCl under the microscope.

Ppt.: $Bi(OH)_3$, $Fe(OH)_3$ Dissolve in HNO_3 Test for Bi^{3+} with stannite solution and with CsCl + KI. Test for Fe^{3+} with $K_4[Fe(CN)_6]$[4]	Solution: AlO_2^-, $CrO_4^=$ Test for Al^{3+} with alizarin and with $KHSO_4$ + CcCl under the microscope. Convert $CrO_4^=$ to CrO_5 and confirm with diphenylcarbazide.

of filter paper is impregnated with a solution of $HgCl_2$ and dried. A drop of test solution is then placed on the filter paper followed by a drop of aniline. A black spot of metallic mercury will appear if Sn^{++} is present. The test for Sn^{++} should be done in the original solution because in the course of the analysis Sn^{++} may be oxidized to Sn^{4+}.

Analysis of Group II

Analysis of Group II is similar to that used in the classical scheme with the added crystal and color reactions. The detection of Ag^+, Hg_2^{++}, and Pb^{++} is carried out on a slide with subsequent examination of crystals under the microscope. Thus, Ag^+ is identified as AgCl recrystallized from ammoniacal solution. Hg_2^{++} is detected by means of $(NH_4)_2[Co(CNS)_4]$ and Pb^{++} is detected by triple nitrite reaction as $K_2Pb[Cu(NO_2)_6]$.[3] Color reactions with diphenylcarbazide for Hg_2^{++} and with dithizone for Pb^{++} are also characteristic and useful.

Table 3. Analysis of Group IV

H_2SO_4 + C_2H_5OH, centrifuged, checked for completness of separation, H^2SO_4 + C_2H_5OH, centrifuged, checked for completness of separation, centrifuged again and residue is washed with ice-cold water.

Precipitate:	Solution:
$BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$	cations of group V and VI.

A portion of the precipitate is heated on a slide with a large drop of water and the solution is removed to the other side of the slide with a micro pipet. A careful evaporation of the solution will form the typical crystals of calcium sulfate. This operation is repeated 2-3 times in order to separate completely $CaSO_4 . 2H_2O$.

The free from Ca^{++} residue is then treated with HCl (1:1) and heated. The hot solution is transferred to another slide. By slow evaporation typical crystals of $SrSO_4$ are formed first, then that of $PbSO_4$. The second extraction with hot HCl will form crytals of $SrSO_4$ and $PbCl_2$. Thus Sr^{++} and Pb^{++} will be identified simultaneously. After the 3rd extraction with hot HCl, the residue (if any) should be only $BaSO_4$ and actually does not need any confirmation. It can be confirmed, however, by conversion of $BaSO_4$ to $BaCO_3$ by fusion with a mixture of Na_2CO_3 + K_2CO_3. The $BaCO_3$ is dissolved in acetic acid and the solution is then tested with sodium rhodizonate and confirmed with $(NH_4)_2[SiF_6]$ under the microscope.

Discussion

The solubility product constants show that the hydroxides or hydrous oxides and basic compounds of metals in the higher oxidation states are less soluble and precipitate at lower pH than those of lower oxidation states. Thus, the $K_{sp}'s$ for $Sn(OH)_4$, $Sn(OH)_2$, $Fe(OH)_3$, and $Fe(OH)_2$ are 1×10^{-56}, 5×10^{-26}, 1×10^{-38}, and 1×10^{-14} respectively. This means that at proper concentration of OH^- hydroxides or basic compounds of the metals of oxidation states + 3 and + 4 may be separated from those of lower charges

TABLE 4. ANALYSIS OF GROUP V

The supernate from Group IV separation is treated with solid NH_4Cl (few mg), made strongly alkaline with NaOH* and heated to boiling, stirred, centrifuged and tested for complete precipitation.

Precipitation: HgO, $Cu(OH)_2$, $Cd(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$ The residue is dissolved in HCl, an excess of NH_4OH is added, the mixture is stirred, and centrifuged.	Solution: Group VI

Precipitate: $HgNH_2Cl$, $Fe(OH)_2$, $MnO(OH)_2$ The original solution was tested for all these ions. Confirm the previous results with the same reagents.	Solution: $Cu(NH_3)_4^{++}$, $Cd(NH_3)_4^{++}$, $Co(NH_3)_6^{++}$, $Ni(NH_3)_6^{++}$ 1) Ni^{++} can be detected by dimethylglyoxime in the presence of all other three ions.

2) Cu^{++} can be identified by potassium ferrocyanide in the presence of all other ions of this subgroup by acidifying the ammoniacal solution with acetic acid.
3) Co^{++} also can be detected in the presence of all other 3 ions in the acidified ammoniacal solution with $(NH_4)_2[Hg(CNS)_4]$. Dark blue crystals typical for Co^{++} appear.
4) Cd^{++} cannot be identified in the presence of other 3 ions. They interfere and should be removed. Cd^{++} is then detected by means of $(NH_4)_2[Hg(CNS)_4]$ under the microscope.
5) Cu^{++} and Cd^{++} can be identified simultaneously in a drop of acidified ammoniacal solution treated with $(NH_4)_2[Hg(CNS)_4]$. In this case the crystals of cadmium will be of a chocolate color.
6) If only Cu^{++} and Co^{++} are present, they also can be detected simultaneously in a drop of the acidified ammoniacal solution with the same reagent. In this case two kinds of crystals are observed: typical dark blue of Co^{++} and yellow-greenish of Cu^{++}.
7) If only Cd^{++} and Co^{++} are present they also can be detected simultaneously in a drop of acidified ammoniacal solution with the same reagent. This time only one type of crystal is formed, that typical for Cd^{++}—long truncated prisms colored dark blue (difference from short prisms and radiates when only Co^{++} is present).

*Carbonate-free

TABLE 5. ANALYSIS OF GROUP VI

Evaporate the solution to dryness. Add water, stir and centrifuge.

Precipitate: $Mg(OH)_2$ Dissolve in HCl, test with magneson, and confirm with $Na_2HPO_4 + NH_4Cl + NH_4OH$	Solution: Sn^{++}, As^{3+}, Zn^{++} Test for Sn^{++} and As^{3+} were made on the original solution. Separate Sn^{++} with NH_4OH and detect Zn^{++} with dithizone in 2N NaOH and with $(NH_4)[Hg(CNS)_4]$

and requiring higher OH^- concentration for the precipitation of their hydroxides.

Therefore, by proper adjustment of pH and utilizing OH^- generated by the hydrolysis of a hot acetate solution it is possible to separate early Bi^{3+}, Sb^{3+}, Sn^{4+}, Fe^{3+}, Al^{3+}, and Cr^{3+}. This will eliminate unexpected or unwanted precipitation commonly associated with these ions during pH changes and no one group will contain so many metals that a complicated subdivision will be required.

Alcohol is added to sulfuric acid to ensure complete precipitation of calcium and strontium sulfates. The separation of Group III is simple and does not cause any complications.

Summary

The proposed system of inorganic qualitative analysis has the following advantages:

1. It employs more specific reactions. It is possible to identify NH_4^+, Na^+, K^+, Mn^{++}, Cr^{3+}, Fe^{++}, Fe^{3+}, Sn^{++}, Sn^{4+}, Pb^{++}, Hg^{++}, As^{3+}, As^{5+} among 26 cations in the original unknown sample.
2. It eliminates the odor and corrosive action of hydrogen sulfide.
3. Major group separation is more sharp (there are no qualitative schemes in which separations are quantitative). Group IV cannot be lost in this scheme.
4. It eliminates punishment of students for not reporting some of the following cations: Cd^{++}, As^{3+}, or As^{5+}, Sn^{++} or Sn^{4+}, Zn^{++}, Ba^{++}, Sr^{++}, Ca^{++}, which can be "lost" easily in the sulfide scheme, no matter how able a student is.
5. It requires fewer reagents than most schemes.
6. Analytical results are much more certain. An average student will make fewer errors.
7. While the essential theory of analysis remains the same, its practical application in the laboratory can be used later in industrial and research laboratory.
8. Lack of fumes and odors and work with microscope and color reactions makes qualitative analysis a more interesting and attractive course.

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